

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

9950-49
Distribution Category UC-63
DOE/JPL-955201-78/1

LOW COST SOLAR ARRAY PROJECT:
Composition Measurements by Analytical Photon Catalysis

Second Quarterly Report

1 January 1979 - 31 March 1979

David G. Sutton, Luis Galvan, James Melzer and Raymond F. Heidner, III

The Ivan A. Getting Laboratories,
The Aerospace Corporation, El Segundo, California 90245

(NASA-CR-158598) LOW COST SOLAR ARRAY
PROJECT: COMPOSITION MEASUREMENTS BY
ANALYTICAL PHOTO CATALYSIS Quarterly
Report, 1 Jan. - 31 Mar. 1979 (Aerospace
Corp., El Segundo, Calif.) 16 p HC A02/MF A01 G3/44
N79-23513
Unclas
25171

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Department of Energy.

JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost Solar Arrays.



Technical Content Statement

This report contains information prepared by the Ivan A. Getting Laboratories of The Aerospace Corporation under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, National Aeronautics and Space Administration or the U.S. Department of Energy.

Table of Contents

	Page
I. Summary	4
II. Background	4
III. Progress During Reporting Period	5
IV. Conclusions	8
V. Future Activity	9
VI. References	10
VII. Figures	11

I. Summary

The object of this research is to assess the applicability of the photon catalysis technique for effecting composition analysis of silicon samples. In particular, our technique is to be evaluated as a detector for the impurities Al, Cr, Fe, Mn, Ti, V, Mo and Zr. During the first reporting period we detected Al, Cr, Fe and Mn with the photon catalysis method. We established the best fluorescence lines to monitor and determined initial sensitivities to each of these elements by atomic absorption calibration. In the course of these tests vapor pressure curves for these four pure substances were also mapped.

During the second quarter we detected Ti and Si with our technique. The best lines to monitor were catalogued and vapor pressure curves were determined. Attempts to detect vanadium were unsuccessful due to the refractory nature of this element and the limited temperature range of our evaporator.

II. Background

Work commenced during the week of September 11 with the assembly of our Analytical Photon Catalysis (MTES)¹ device into a configuration suitable for the study of silicon impurities. The resulting instrument and its function can best be explained with reference to Figure 1. It consists of a vertical section of quartz tubing 9 cm in diameter. An electrically heated metal vapor furnace is attached to the bottom of the quartz tube, and a 60-l/sec pump, attached at the top of the quartz tube, provides the means to evacuate the system. Argon or nitrogen injected through the bottom of the furnace assembly entrains the flow of metal atoms from the furnace and carries it into the quartz observation section. In this section, the concentration of argon is much greater than the metal concentration. A thermocouple placed in contact with the metal in the furnace allows direct measurement of the metal atom source temperature, or an optical pyrometer may be employed by observing the heated metal down through the observation window.

A ring-shaped quartz gas injector is inserted into the apparatus at the junction of the furnace assembly and quartz flow tube. Through this injector, active nitrogen is introduced into the Ar-metal atom stream. The active nitrogen, consisting primarily of N atoms, $N_2(A^3\Sigma_u^+)$, and ground-state N_2 , was prepared upstream of the injector by passing N_2 gas through a 70-W microwave discharge. The region of the quartz flow tube approximately 5 cm above the active nitrogen injector is monitored photoelectrically with an uncooled RCA 1P28 phototube attached to a one meter monochromator. Apart from neutral density filters, which are used at higher metal concentrations to avoid high photomultiplier tube current, no other optics are used. Hollow-cathode lamps can be placed on the opposite side of the flow tube and at the same height as the monochromator entrance slits. They are used as a line source for the atomic absorption measurements to calibrate the fluorescence intensity measurements with respect to metal vapor concentration.

The Ar and N_2 flows are adjusted to give a total pressure of 2-4 Torr. With the microwave generator set to deliver 70 W to the N_2 flow, a pale straw-colored glow is observable downstream of the injector. The furnace is then set to a given temperature, and the resulting atomic line emission intensities are measured.

The most intense and spectroscopically isolated lines are chosen (in accordance with Task 1A of the statement of work) to be the best fluorescence lines to monitor for the purposes of analysis. The intensity is a direct measure of the concentration of the emitting species and can be calibrated as specified in Task 1B at high source temperatures by the atomic absorption technique. If one plots the $\log I$ vs $10^4/T(K)$ a vapor pressure curve results as per Task 1C. These three tasks applied to Al, Cr, Fe and Mn occupied us for the first quarter. During the second quarter we completed Tasks IABC by our examination of titanium, vanadium and silicon.

III. Progress During Reporting Period

During the month of January we completed our testing of titanium. We show in Figures 11 and 12 the MTES spectrum and the vapor pressure curves for this element, respectively. The titanium spectrum consists of groups of triplets. The most intense individual lines occur at 365.3, 398.2, 399.0 and 399.9 nanometers. The two aluminum peaks that appear are due to the presence of foil that serves as a reflector. Inadvertently it was placed too close to the heater element and some of it was vaporized. This problem has since been eliminated by redesigning the oven section and switching to tantalum foil. Blank experiments done with empty crucibles now show only traces of sodium even at the highest temperatures. The sodium is presumably introduced as an impurity in the crucible. The signal due to this element rapidly diminishes on bake-out. An example of a blank experiment showing the spectrum obtained with an empty crucible is given in Figure 13.

Figure 12 summarizes our temperature dependent measurements at two different wavelengths, 365.3 and 399.8 nm. The data at both wavelengths are fit with straight lines calculated with a least squares fitting routine. The slopes of both lines are also determined in this process. They agree to within 3% and 7% with Hultgren's² recommended data. This excellent agreement is consistent with the high purity quoted for our titanium sample and verifies the accuracy of our calibration technique.

Attempts to calibrate Figure 12 using atomic absorption were unsuccessful. We can estimate the lowest concentrations observed with the rate of vaporization method outlined previously. The lowest temperature that still resulted in a measurable signal was 1285°K. At this temperature titanium sublimes⁶ at a rate of approximately 8×10^{-11} grams/cm²-sec. If we have identical sensitivities for Ti and Bi then our lowest signal for titanium corresponds to a Ti concentration of less than 10^4 atoms/cm³. The highest temperature our oven is capable of sustaining is 1590°K. The rate of vaporization method enables us to estimate our Ti concentration at this temperature to be between 10^6 and 10^7 atoms per cm³ in our observation region. These low values are consistent with the null signal we obtained in our atomic absorption experiments³, since this method is normally insensitive to concentrations less than 10^8 per cm³.

During the month of February we attempted to detect vanadium vapor in our MTES apparatus. As anticipated the temperature obtainable from our oven was insufficient to yield a signal from vanadium. We can estimate a lower limit to the sensitivity for vanadium using the rate of evaporation technique discussed in the first quarterly report (Dec. 1979). This estimating procedure places the lower limit of detection for vanadium at 10^5 atoms per cm^3 in the gas phase. No atomic absorption experiments were attempted, since such a low concentration is incompatible with detection by this classical method.

Our digital thermocouple finally arrived along with the circuit board to provide accurate readout. Installation of this instrument will eliminate the tedious temperature measurement routine required by use of the optical pyrometer. In addition, no correction procedure is required, the thermocouple is inherently more accurate and the opportunity for errors is reduced.

Since a null result was achieved with vanadium we attempted several preliminary experiments with Si. In particular, with NBS Standard Reference Material #57 (SRM57). The analysis supplied by NBS for this material is reproduced below.

SRM57
Chemical Composition (Weight Percent)

Mn	P	S	Si	Cu	Ni	Cr	Ti	Al	Zr	Ca	Mg	Fe
0.034	0.008	0.005	96.8	0.02	0.002	0.025	0.10	0.67	0.025	0.73	0.01	0.65

We can see that SRM57 is not particularly pure material. It does have the advantage, however, of containing a large number of the impurities that concern this investigation, and it is an NBS standard so that one may have confidence in the supplied analysis. Since this material contains over 3% impurities, we might expect some segregation and fractional distillation as the Si is melted and vaporized. This behavior would manifest itself in vapor pressure curves that would vary from the vapor pressure curve of the host matrix, silicon. This hypothesis will be tested on SRM57 by measuring the vapor pressure curves of Si and as many impurities as practical simultaneously. If all the vapor pressure curves are identical, we have proof that the vaporization process is congruent and measurement of the vapor composition will reflect the composition of the silicon sample.

During March we analyzed the rich spectrum resulting from Si SRM57. Shown in Figure 14 is a portion of this MTES spectrum. In addition to the Si lines near 250 nm and 288 nm we can easily identify spectral lines from the following elements:

Element	Wavelength of Prominent Lines Observed from SRM57, nm
Si	251.6, 288.2
Al	308.2, 309.2
Cr	359.4, 425.4
Mn	279.5, 403.1
Fe	239.5 (?)
Mg	285.2
Cu	324.7, 515.3
Na	330.2 (background impurity)
Ca	422.7, 487.8

In order to prove that the vaporization process is occurring at a rate determined by the silicon matrix, we are constructing apparent vaporization curves for most of these impurities, using SRM57 as the vapor source. Data is accumulated simultaneously on the intensities of the fluorescence lines due to impurities as well as the silicon 251.6 nm line. These data are plotted on semilog paper as a function of the inverse of the source temperature. These apparent vaporization curves are compared with the silicon curve and with the vapor pressure curves obtained by the previous work with pure metal sources.

An example of our analysis is shown in Figure 15. The solid lines on this plot connect data points obtained at 251.6, 422.7 and 309.2 nm and track Si, Ca, and Al, respectively. These three curves were established simultaneously using Si SRM57 as the source of the vapor. For comparison the vapor pressure curves obtained earlier for Al and Ca using the pure metal as a vapor source are plotted on the same graph as dashed lines. One easily discerns a trend for the apparent vapor pressure curves of the impurities (Al, Ca) to parallel the curve of the host matrix (silicon). This is powerful evidence that the evaporation process is congruent, and thus, analysis of the vapor via MTES will reflect the composition of the original solid sample.

The significance of this milestone is perhaps best expressed mathematically. If the evaporation process is congruent, the composition of the vapor will be constant (i.e., the same as the source). Consequently, the ratio of MTES fluorescence intensities due to an impurity, i , and silicon will be constant

$$\frac{I_i}{I_s} = C \quad (1)$$

Take the log of both sides of (1) to get

$$\log I_i - \log I_s = \log C \quad (2)$$

For the host Si matrix the MTES vapor pressure curve is linear in inverse temperature.

$$\log I_s = \frac{a}{T} + b \quad (3)$$

Substituting (3) into (2) gives

$$\log I_i = \frac{a}{T} + b + \log C \quad (4)$$

By comparison of equations (3) and (4), we see that plots of $\log I_i$ and $\log I_s$ vs. $1/T$ would have the same slope, a . This behavior is observed in Figure 15 and is seen to be a direct consequence of congruent evaporation.

IV. Conclusions

Based on these results we can expand our previous table by two columns. This is done below. The complete table summarizes our findings under Task IABC. Our MTES technique appears to be very sensitive to titanium. While we can't be precisely quantitative the sensitivity seems comparable to Al, Cr and Mn.

element	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Mn</u>	<u>Ti</u>	<u>V</u>	<u>Si</u>
best MTES lines (nm)	309.2, 396.1	359.4	344.1	279.5	399.8		251.6
ancillary lines (nm)	308.2, 394.4	347.9, 425.4	358.1, 372.0	403.1	365.3		288.3
sensitivity (cm ⁻³)	3 x 10 ⁵	2 x 10 ⁵	10 ⁷	5 x 10 ⁴	10 ⁴	>10 ⁵	
projected sensitivity in Si Matrix (ppb)	30	20	1000	5	1	>10	

Our preliminary results with Si (SRM57) show that qualitative analysis is easily accomplished with MTES. In addition, the "best lines" established with use of the pure materials are seen to be invariant with matrix, suggesting that the excitation process occurs independently for each species present in the vapor. If this proves to be the case, then cooperative and matrix effects (interferences) will be minimal.

The vapor pressure curves measured for Si, Al and Ca with Si (SRM57) as the source suggest very strongly that our MTES measurements in the vapor phase will be simply and directly related to the composition of the solid sample.

V. Future Activity

As per the program plans we intend to investigate the NBS silicon sample more thoroughly. In particular, we will measure additional vapor pressure curves for impurities in SRM57. Due to the large number and high percentage of impurities in this material it will also serve as a source for our study of interferences, both optical and chemical. The effects of selective evaporation can be evaluated by repeating our vapor pressure curve analysis with samples of higher purity. We have obtained samples from SPEX Industries with measured impurities at the ppm level. These will be evaluated in the same manner as SRM57. In addition, we hope to begin our analysis of samples supplied by JPL near the beginning of June. Special attention will be given during these studies to define optimal running conditions for Al and Cu. These two elements are common to all three samples. Thus, the beginnings of an analytical curve for these two elements could be established by data taken under identical conditions using the three samples (NBS, SPEX, JPL) as standards.

VI. References

1. The term Metastable Transfer Emission Spectrometry, MTES, is somewhat more descriptive and is used synonymously with Analytical Photon Catalysis. See Rev. Sci. Instrum. 49, 1124 (1978).
2. Ralph Hultgren, et al., "Selected Values of Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc. (New York, 1963).
3. An. N. Nesmeyanov, "Vapor Pressures of The Elements," translated and edited by J.I. Carasso, Academic (New York, 1963).
4. C.H. Corliss and W.R. Bozman, "Experimental Transition Probabilities for Spectral Lines of Seventy Elements," (NBS Monograph 53, 1962).
5. M. Pinta, "Detection and Determination of Trace Elements," Ann Arbor Science Publishers, Inc. (Ann Arbor, Mich., 1962).
6. S. Dushman, "Scientific Foundations of Vacuum Technique," edited by J.M. Lafferty, John Wiley and Sons, Inc. (New York, 1962).

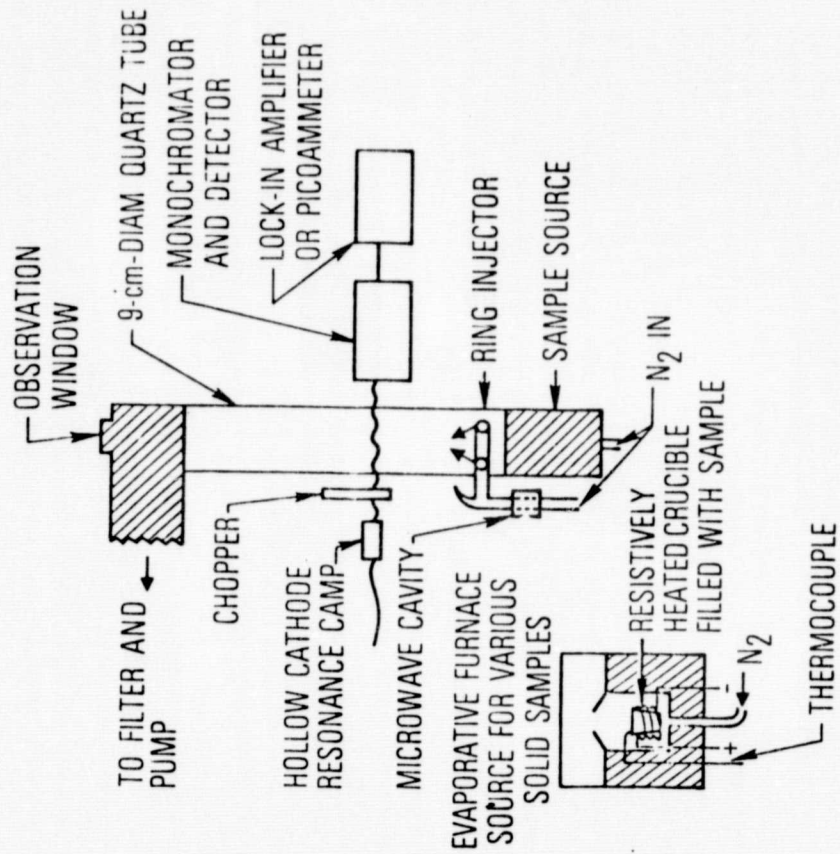


Figure 1: Schematic for MTES Apparatus

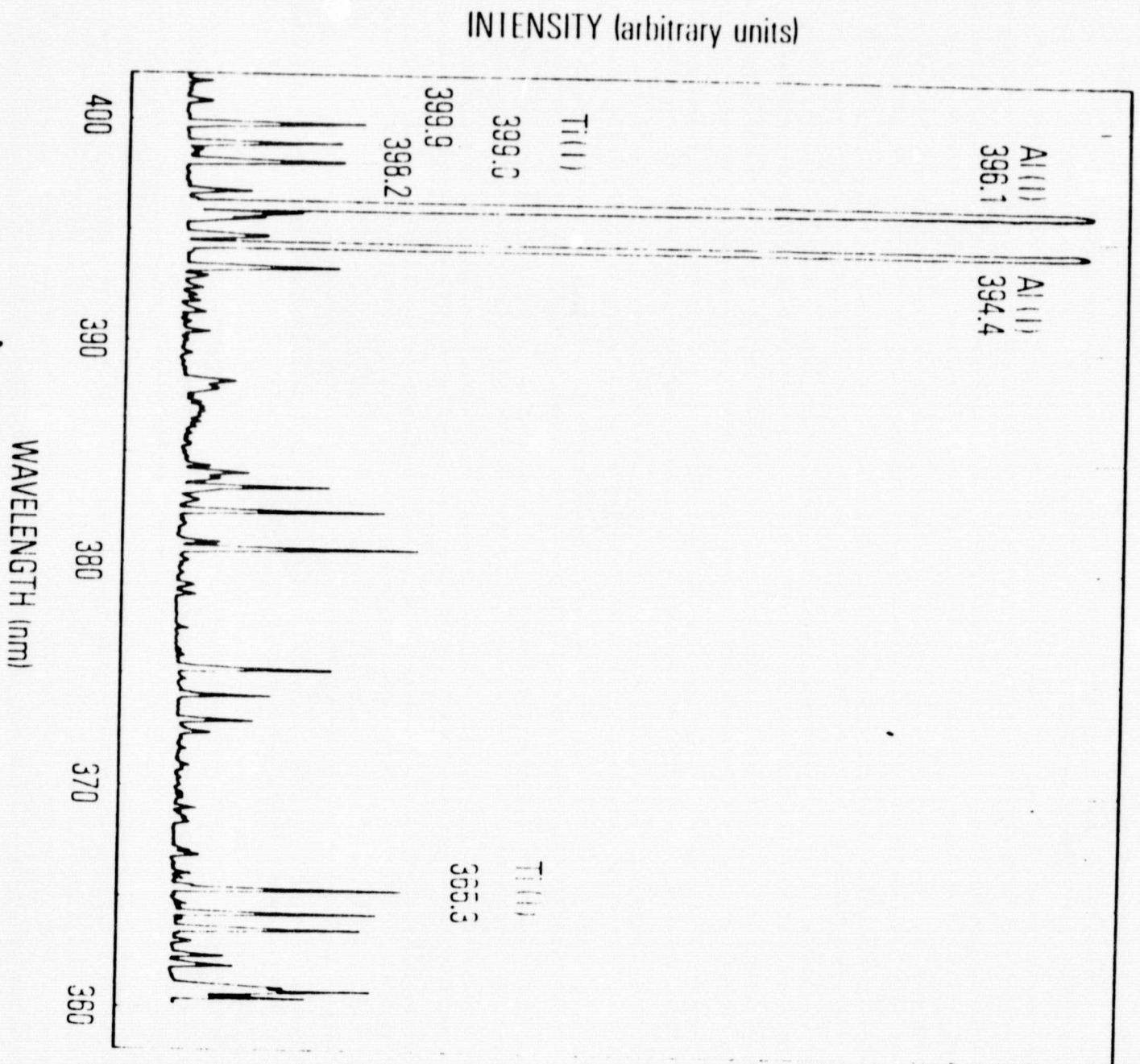


Figure 11: MPS Spectrum for Titanium

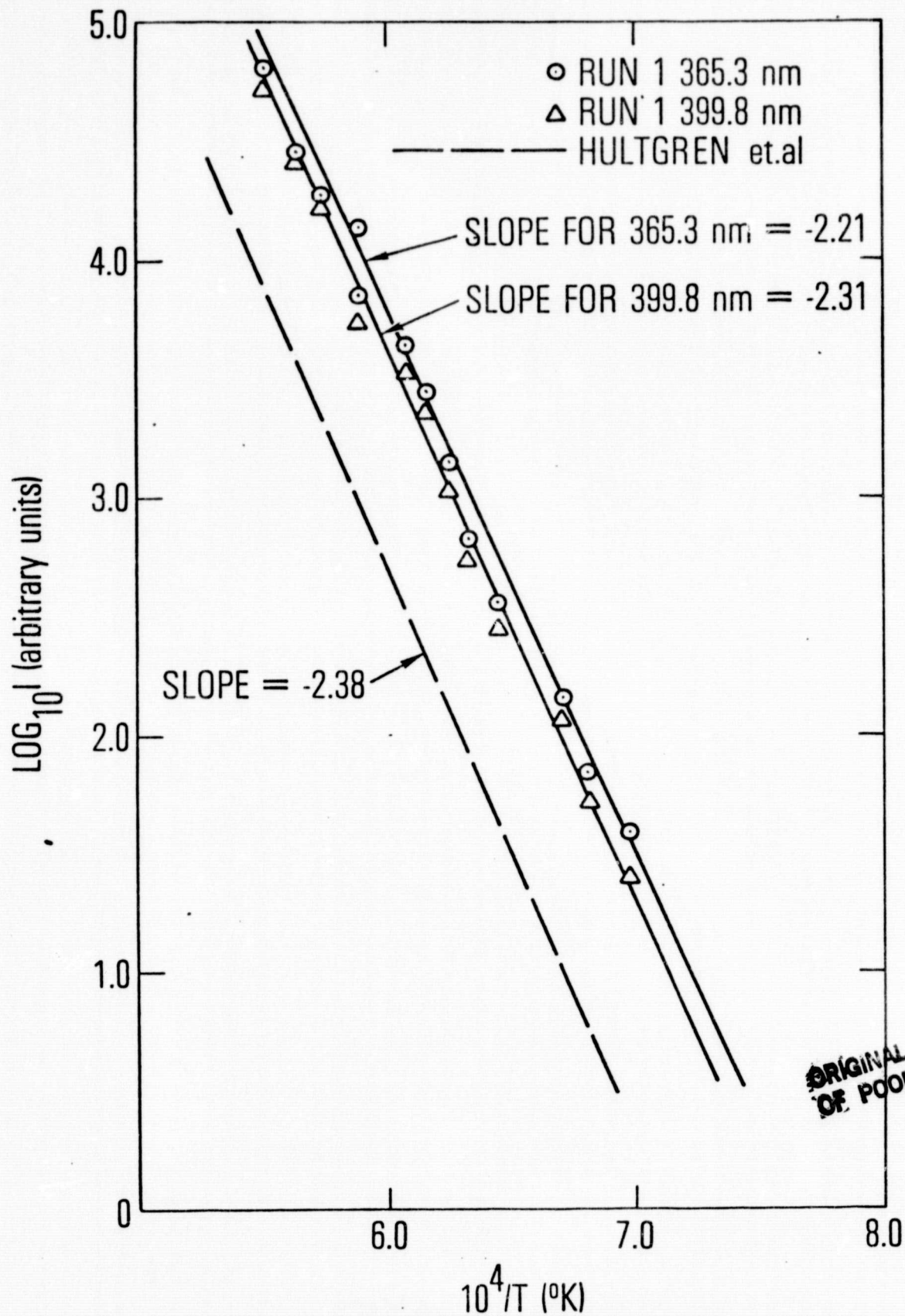


Figure 12: MTES Vapor Pressure Curve for Titanium

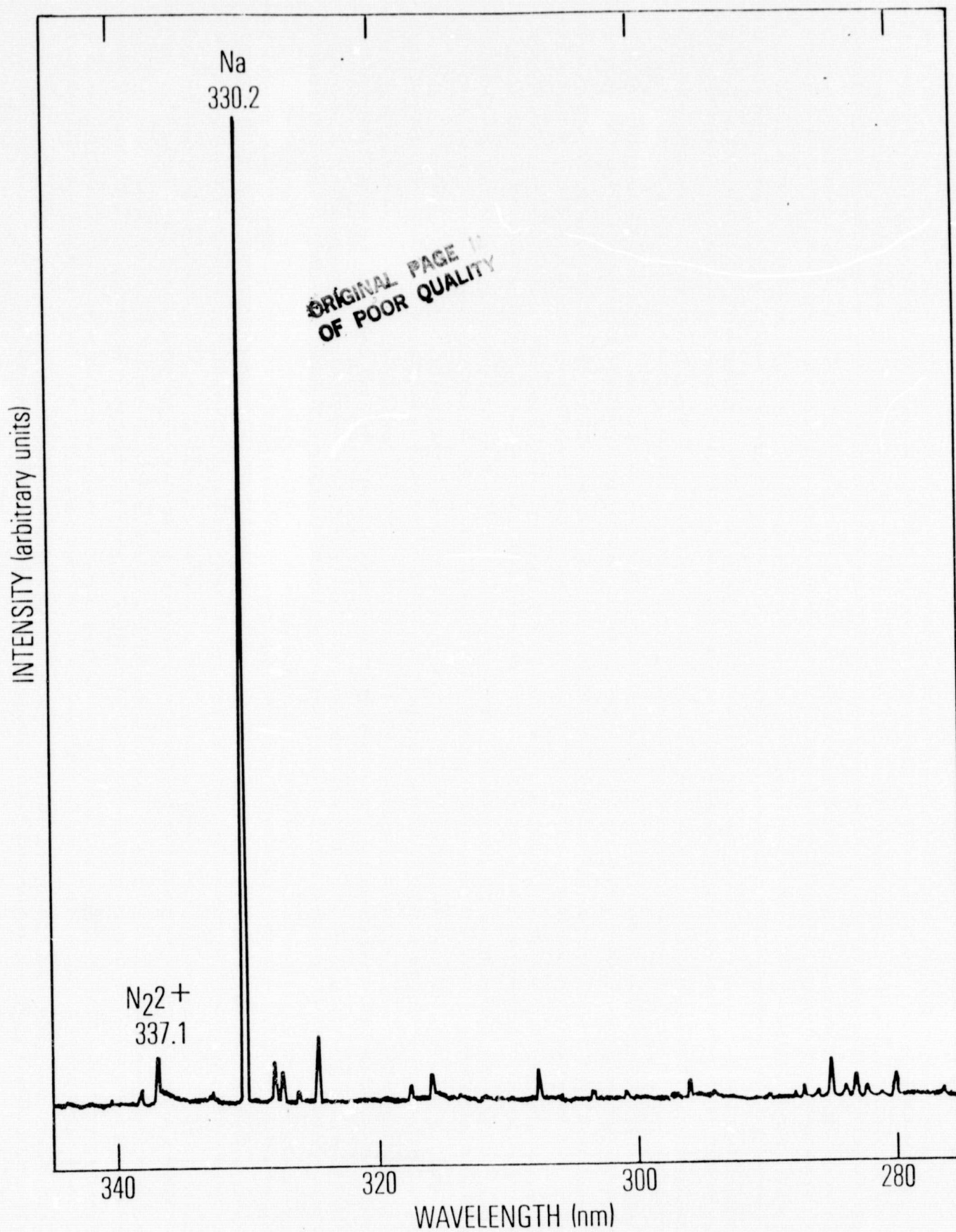


Figure 13: MTES Spectrum Obtained with Empty BeO Crucible

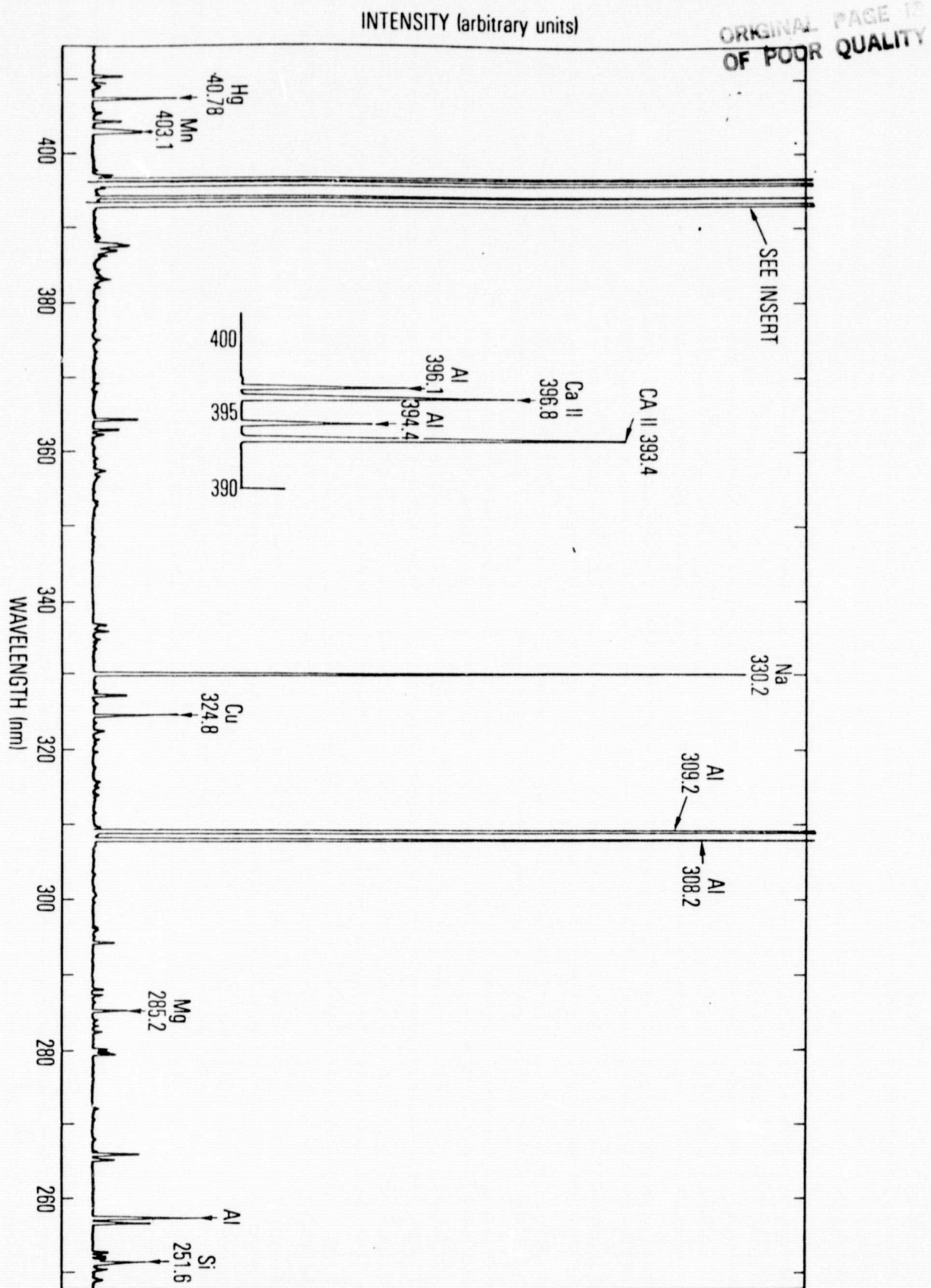


Figure 14: Partial MTES Spectrum for Si(NBS-SRM57)

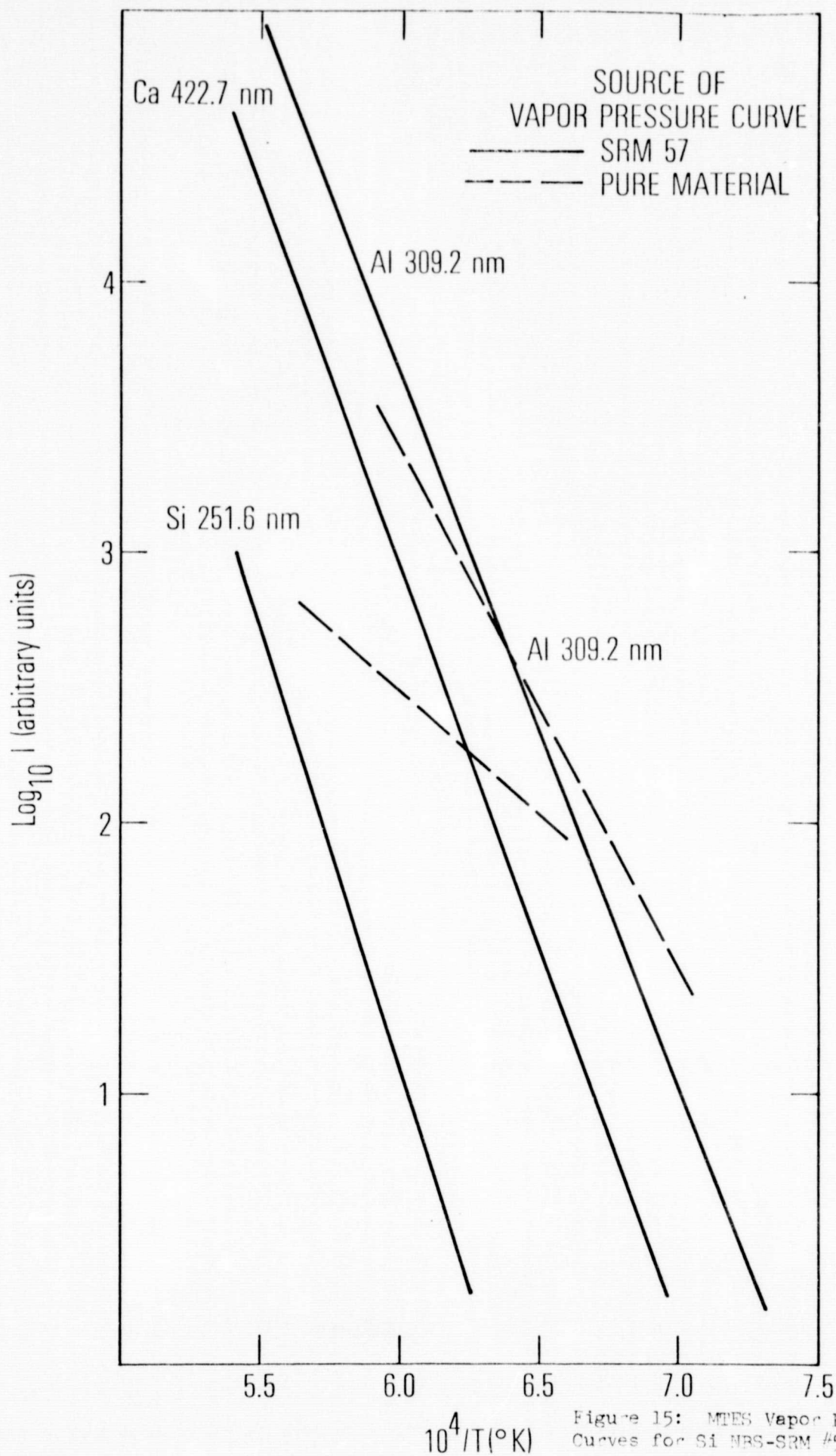


Figure 15: MPES Vapor Pressure
Curves for Si NBS-SRM #57